Available online at www.sciencedirect.com

ScienceDirect

Procedia Computer Science 57 (2015) 160 – 167

Procedia Computer Science

2013 International Conference on Computational Science

Computational Electronic Study of ScS

Purvee Bhardwaj and Sadhna Singh

High pressure Research Lab., Department of Physics, Barkatullah University, Bhopal-462026, India.

Abstract

Pressure-induced structural and electronic properties of ScS have been investigated. These properties have been studied using first principle calculations as well as interionic potential model modified with covalency effect. Gibbs free energy and enthalpy calculations show that present compounds undergo a structural phase transition from NaCl-type structure to CsCl-type structure. The electronic band structure and density of states of the ScSe have also been reported. The calculated equilibrium structural parameters are in good agreement with the available experimental results.

Peer-review under responsibility of organizing committee of the 3rd International Conference on Recent Trends in Computing 2015 (ICRTC-2015)

Keywords: Phase transition; Electronic properties; Volume collapse.

1. Main text

In the group of rare earth compounds (REC), the pnictides and chalcogenides have attracted attention due to the presence of strongly correlated f-electrons in them. The nature of these f-electrons can be changed from localized to itinerant leading to significant changes in physical and chemical properties of REC under the effect of pressure. Many rechargeable batteries are made with rare earth compounds. Rare earths are used as catalysts, phosphors, and polishing compounds. The structural, electronic, and high-pressure properties of REC make

* Corresponding author. Tel.: +91 0755 2517115; fax: +91 0755 2677723.
E-mail address: purveebhardwaj@gmail.com

Peer-review under responsibility of organizing committee of the 3rd International Conference on Recent Trends in Computing 2015 (ICRTC-2015)
doi:10.1016/j.procs.2015.07.409

them candidates for advanced industrial applications which include magnetic, alloys, catalysts, ceramics, glass, nuclear, and phosphors. They provide unique physical properties For these applications, which cannot be achieved with other materials [1-3].

Among these RECs the rare earth chalcogenides undergo a pressure induced electronic phase transition during the high-pressure resistivity studies [4]. For some rare earth chalcogenides this transition is found to be continuous while discontinuous for others. The compressibilities of the rare earth monochalcogenides have been investigated up to 300 kbar using high-pressure x -ray-diffraction techniques by Chatterjee et. al. [5]. The electronic collapse involving the promotion of a 4f electron into 5d state at high pressure is observed by Jayaraman et. al. [6]. Lately, Maachou et. al. [7] reported the high-pressure structural (B1–B2) phase transition and the elastic properties of ScS using the full-potential augmented plane wave plus local orbitals method (FP-APW + LO) with the generalized-gradient approximation (GGA) exchange-correlation functional. The scandium chalcogenide ScS is the least studied material of rare earth chalcogenide family. Experimental and theoretical studies of ScS under pressure have been reported by Peiris et. al. [8]. Only few papers are reported in the literature to know the properties of ScS [7-9].

The lack of this information motivated us to explore the structural and electronic properties of ScS compound. In the present article, the structural and electronic properties are investigated using two approaches: the model calculation (Approach I) and first principle calculations (Approach II). The ground state properties for B1-type ScS are studied by the first principle tight binding linear muffin tin orbital (TB-LMTO) method. The comparative study of structural phase transition and volume collapse of present chalcogenide has been reported from both approaches. We further report the electronic band structure (BS) and density of states (DOS) for ScS. The organization of this article is as follows: In Section 2 the method of computation of both the approaches is described. The Modified interaction potential model (MIPM) with including covalency effect is described in Section 2.2. In Section 3, results are discussed. In subsections 3.1 and 3.2 the structural and electronic properties of ScS at ambient and high pressure are presented respectively. At last, in Section 4, we have concluded the results.

2. Methods of Calculation

2.1. First Principle calculation

The present scandium chalcogenide considered in the present work crystallize in NaCl-type (*Fm3m, 225*) structure at ambient conditions. The scandium atom is positioned at (0,0,0) and sulfide at (1/2,1/2,1/2). Under pressure they transform to CsCl-type (*Pm3m, 221*) structure in which the polonium is positioned at (1/2,1/2,1/2). For loosly packed structures, empty spheres are introduced in the appropriate intensities in NaCl phase without breaking the crystal symmetry. Since the TB-LMTO method works well for the closed packed structures, while the present compounds belongs to NaCl phase at ambient condition, which is not a close packed one. Therefore for these loosely packed structures the two equivalent empty spheres at position (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) have been introduced in such a way that they do not break the crystal symmetry [10]. For CsCl structure these empty spheres are not needed because it is a closed packed structure. The electronic band structures are calculated the self-consistent tight binding linear muffin tin orbital (TB-LMTO) method [11,12] within the local density approximation (LDA) [13]. Van Barth and Hedin [14] parameterization scheme has been used for the exchange correlation potential. To minimize the errors in LMTO method combined correction terms are included. The partial waves of s p d and f states are taken into account. The E and k convergences are checked subsequently to achieve better accuracy. The calculations were performed for 512 k points (grid of 8×8×8) in the Brillouin zone for both the B1 and B2 phases. To

obtain the total energy and partial density of states the tetrahedron method [15] of Brillion zone integration is used. The total energy was computed by reducing the volume from 1.05 V_0 to 0.60 V_0, where V_0 is the equilibiurum cell volume. The calculated total energy was fitted to Birch equation of state [16] to obtain the pressure volume relation. The pressure is obtained by taking the volume derivative of total energy. The bulk modulus B (= $-V_0 dP/dV$) is also calculated from the P-V relation. The stability of a particular structure is decided by the minima of the enthalpy. The phase transition pressure can be obtained by matching enthalpies of both structures such that the difference of enthalpy ΔH (=H_{B2}- H_{B1}) becomes zero at transition pressure.

2.2. Model Calculation

The natural consequence of application of pressure on the crystals is the compression, which in turn leads to an increased charge transfer (or three-body interaction effects) [17] due to the existence of the deformed (or exchanged) charge between the overlapping electron shells of the adjacent ions. These effects have been incorporated in the Gibbs free energy (G = U+PV-TS) as a function of pressure and three body interactions (TBI), which are the most dominant among the many body interactions. Here, U is the internal energy of the system equivalent to the lattice energy at temperature near zero and S is the entropy. At temperature T=0K and pressure (P) the Gibbs free energies for BX (X=1,2) phase is:

$$\begin{aligned} G_{BX}(r) = & \frac{-\alpha_M{}^X Z^2 e^2}{r^X} - \frac{12\alpha_M{}^X Z e^2 f_m(r)}{r^X} - [\frac{C^X}{r^{X6}} + \frac{D^X}{r^{X8}}] \\ & + 6b\beta_{ij}\exp[(r_i + r_j - r^X)/\rho] + 6b\beta_{ii}\exp[(2r_i - Y_X r^X)/\rho] \\ & + 6b\beta_{jj}\exp[(2r_j - Y_X r^X)/\rho] + PV_{BX}(r^X) \end{aligned} \quad (1)$$

Where X= 1 (Phase 1=B1), 2(Phase 2=B2), and Y_x= 1.414, 1.154, for NaCl (B1) and CsCl (B2) structures respectively.

With $\alpha_m{}^X$ as the Madelung constant. C and D are the overall van der Waal coefficients for NaCl and CsCl structure respectively, β_{ij} (i,j=1,2) are the Pauling coefficients defined as $\beta_{ij}=1+(Z_i/n_i)+(Z_j/n_j)$ with Z_i (Z_j) and n_i (n_j) as the valence and the number of electrons of the i(j)th ion. Ze is the ionic charge and b (ρ) are the hardness (range) parameters, r is the nearest neighbour separations $f_m(r)$ is the modified three body force parameter which includes the covalency effect with three body interaction, r_i (r_j) are the ionic radii of ions i (j).

These lattice energies consist of long range Coulomb energy (first term), three body interactions corresponding to the nearest neighbour separation r (second term), vdW (van der Waal) interaction (third term), energy due to the overlap repulsion represented by Hafemeister and Flygare (HF) type potential and extended up to the second neighbour ions (fourth, fifth and sixth terms). Covalency effect has been included in the second term of energy [17-19].

3. Result and Discussion

3.1. Structural Properties

When Gibbs free energy difference ΔG approaches zero (ΔG→0) the phase transition is occurred. At phase transition pressure (P_t) present chalcogenide undergoes a (B1-B2) transition associated with a sudden collapse in volume showing a first order phase transition. Fig.1 shows our present computed phase transition pressure for B1-B2 structural transition in ScS at 84.5 GPa from approach I. The present phase transition pressure has been illustrated by arrow in Fig. 1 and has been listed in Table-2 along with the comparisons with the available results [7]. It is interesting to note from the Table-2 and Fig. 1 that the phase transition pressures (P_t), obtained from the MIPM model are in good agreement with the available results [7]. We have also computed the relative volume changes V(P)/V(0) corresponding to the values of *r* and *r'* at different pressures and plotted them against the pressure for ScS. It is clear that during the phase transition from NaCl to CsCl, the volume discontinuity in pressure volume phase diagram. Fig. 2 represents the volume collapse at the phase transition pressure. The calculated value of volume collapse is 4.98%.

Table-1 Input and output parameters of Scandium chalcogenide.

Crystal	Input parameters		Output parameters		
	r (Å)	B (GPa)	b	ρ	f_m (r)
ScS	2.605[a]	115[a]	12.7563	0.269	0.00147

a-ref [7].

Table-2 Phase transition and volume collapse of ScS.

Crystal	Phase transition pressure (GPa)		Volume collapse (%)	
	Present	Others	Present	Others
ScS (Approach I) (Approach II)	 84.5 86.0	 87.25[a]	 4.98 5.10	 5.29[a]

a-ref [7]

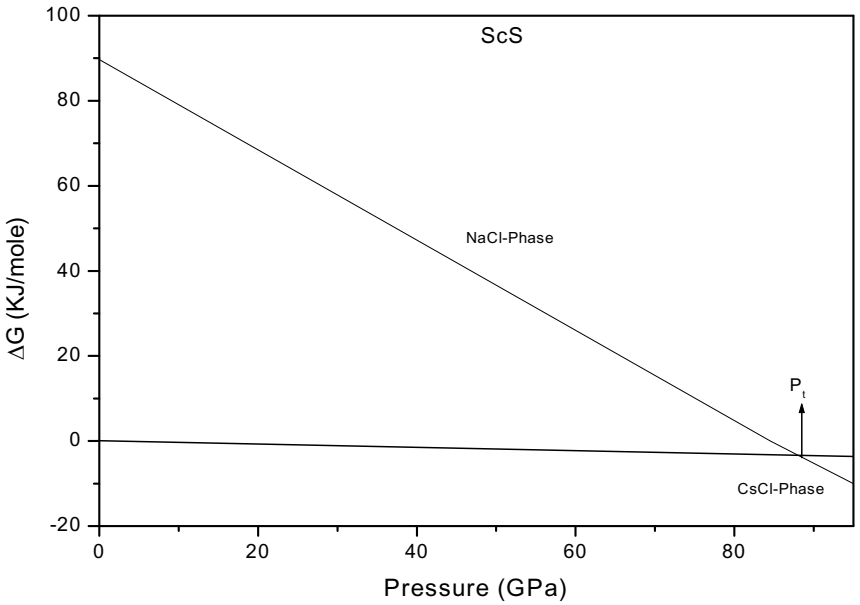

Fig: 1 Variation of Gibbs free energy change ΔG (KJ/mole) with pressure for ScS.

The electronic band structures BS calculations are performed to estimate the total energy of scandium sulfide by using the first principle TB-LMTO method. The minimum of total energy define the equilibirium volume V_0 (or equilibirium a_0), which are found to **be Å^3** for ScS and the corresponding parameters is 5.185Å which is underestimated by 5.1%. These values have been compared with available data. The calculation of phase transition pressure is carried out by estimating enthalpy in both the structures as described earlier given in Section 2. At the phase transition pressure where the enthalpies of two phases become same, both the phases coexist. The calculated value of phase transition pressure is 86.0GPa for the present compound and it is compared with other theoretical results [7] in Table-2

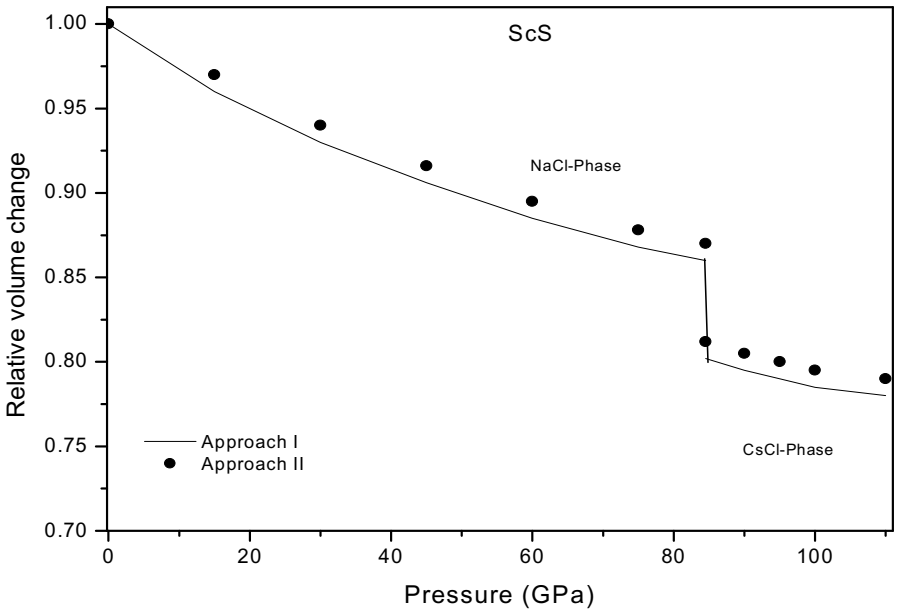

Fig: 2 Relative volume changes versus pressure. Solid line and solid circles represent approach I and approach II respectively for ScS.

3.2. Elastic Properties

The elastic properties provide information on the stability and stiffness of a material. These properties are also useful for industrial applications. We have calculated the values of bulk modulus and pressure derivatives of bulk modulus from both approaches.

The computed value of bulk modulus [$B = (C_{11}+2C_{12})/3$] and pressure derivative of bulk modulus (B') are given in Table-3. The hardness of a material can be determined more accurately by using the Bulk modulus. The calculated value of bulk modulus of ScS from first principle calculation is also presented in Table-3. Our calculated value of bulk modulus for ScS is 110.5 (112.7) GPa for NaCl-phase and 114.01 (116.34) GPa for CsCl-phase for approach I (approach II) respectively. These data have been compared with theoretical [7] and experimental results [20]

Table-3 calculated equilibrium lattice parameter a (Å), bulk modulus B (GPa) and pressure derivative of bulk modulus of ScS.

Properties	ScS	
	NaCl-type	CsCl-type
Lattice parameter (Å)		
Present (Approach I)	5.205	3.104
(Approach II)	5.185	3.126
Others	5.2101[a]	3.158[b]
Expt.	5.199[b]	-
Bulk modulus (B) (GPa)		
Present (Approach I)	110.5	114.01
(Approach II)	112.7	116.34
Others	115.33[a]	118.52[a]
Expt.	103±11[b]	-
Pressure derivative of bulk modulus (B')		
Present (Approach I)		
(Approach II)	3.15	3.32
Others	3.36	3.56
	3.51[a]	3.665[a]

a-ref [7], b-ref [20]

3.3. Electronic Properties

The electronic band structure (BS) and density of states (DOS) shown in Fig. 3 for ScS respectively in their parent phase under ambient condition. It is clearly seen from this figure that the present compound shows the metallic behaviour as reported earlier in the literature [7]. Since present compound undergoes a B1 to B2 phase transition so to study the mechanism of transition, we have also investigated the electronic structure at high pressures in CsCl (B2) phase. It is found that the present material shows metallization under high pressure. The band structure in high-pressure B2 phase is reported in Fig. 4. More compressed bands are seen in CsCl (B2) phase.

4. Conclusion

We have studied the electronic band structure and phase transition properties of the ScS chalcogenide from two approaches I [modified interaction potential model (MIPM)] and approach II [first principle tight binding linear muffin tin orbital (TB-LMTO) method]. The present results show that the equilibrium lattice constants,

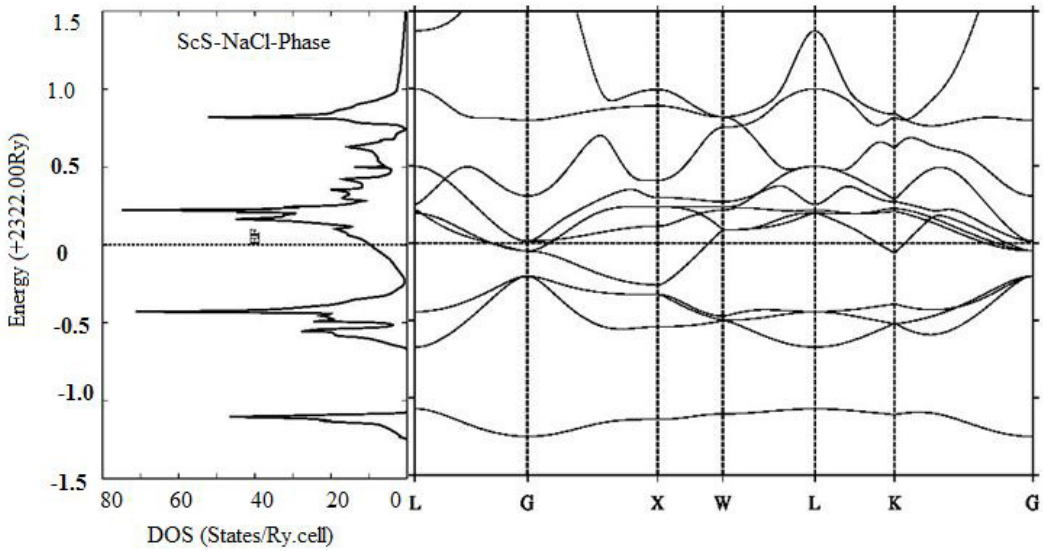

Fig: 3 Electronic Band structure (BS) and total density of States (DOS) of ScS in NaCl phase.

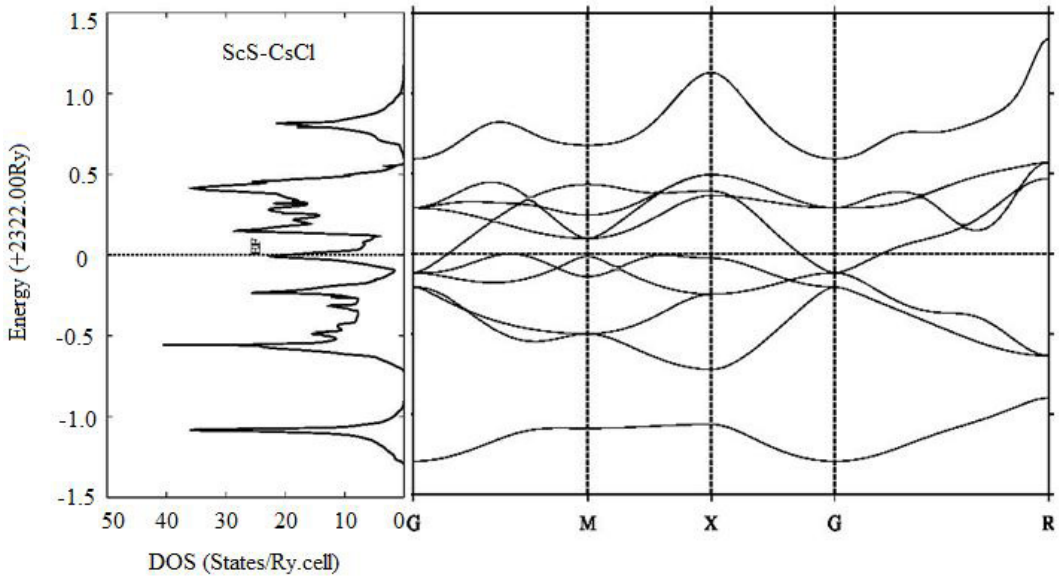

Fig: 4 Electronic Band structure (BS) and total density of States (DOS) of ScS in CsCl phase.

bulk modulus and pressure derivative of bulk modulus from both the approaches are in good agreement with experimental and other theoretical data. The B1 and B2 phase transitions have been fruitfully calculated by both the approaches. To understand the electronic structure present compounds show metallic behavior.

Acknowledgement

Authors are thankful to Department of Science & Technology (DST), New Delhi for the financial support to this work. One of the authors (PB) is grateful to Department of Science & Technology (DST), New Delhi for, awarding WOS-'A' (Grant no SR/WOS-A/PS-17/2013).

References

[1]. C. Coban, K. Colakoglu, Y.O. Ciftci, Mater. Chem. Phys. 2011; **125** pp. 887-894.
[2]. D.X. Li, Y. Haga, H. Shida, T. Suzuki, Y.S. Kwon, Phys. Rev. B 1996; **54** pp. 10483-10491.
[3]. M. Yoshida, K. Koyama, T. Sakon, A. Ochiai, M. Motokawa, J. Phys. Soc. Jpn. 2000; **69** pp. 3629-3632.
[4]. A. Jayaraman, V. Narayanamurti, E. Bucher, R.G. Maines, Phys, Rev. Letter, 1970; **25** pp. 1430-1433.
[5]. A. Chatterjee, A. K. Singh, and A. Jayaraman, Phys. Rev. B 1972; **6** pp. 2285-2291.
[6]. A. Jayaraman, Indian J of Pure & Applied Physics 1971; **9** pp. 983-985.
[7]. A. Maachou, H. Aboura, B. Amrani, R. Khenata, S. Bin Omran, Dinesh Varshney, Computational Materials Science 2011; **50** pp. 3123.
[8]. S. M. Peiris, T. Michael Green, L. Dion Heinz, K. Jeremy Burdett, Inorg. Chem. 1996; **35** pp. 6933-6936.
[9]. F. Hulliger, G.W. Hull Jr, Solid State Commun. 1970; **8** pp. 1379-1382.
[10]. N.E. Christensen, Phys. Rev. B 1985; **32** pp. 207-228.
[11]. The source of the computer code can be downloaded with permission from Prof. Andersen 5Andersen@and.mpi-stuttgart.mpg.de4. However, documentation about the installation and run of the TB-LMTO code can be downloaded from the website: cst-5www.nrl.navy.mil/users/mazin/LMTODOC.pdf4; O.K. Andersen, Linear methods in band theory, Phys. Rev. B. 1975; **12** pp. 3060-3083.
[12]. O. K. Andersen and O. Jepsen, Phys. Rev. Lett. 1984; **53** pp.2571-2574.
[13]. W. Kohn and L.J. Sham, Phys. Rev. A 1965; **140** pp. 1133-1138.
[14]. U. Van Barth and L Hedin, J. Phys. C 1972; **5** pp. 1629-1642.
[15]. O. Jepsen and O.K. Andersen, Solid State Commun. 1971; **9** pp. 1763-1767.
[16]. F. Birch, J. Geophys. Rev. 1978; **83** pp. 1257-1266.
[17]. P. Bhardwaj and S. Singh, phys. status solidi b, 2012; **249** pp. 38-49.
[18]. S. Singh, P. Bhardwaj, J. Alloys Compd. 2011; **509** pp. 7047-7051.
[19]. P. Bhardwaj, M. Sarwan, R. Dubey and S. Singh, J of Mol. Struc. 2013; **1043** pp. 85-90.
[20]. A. Svane, P. Strange, W.M. Temmerman, Z. Szotek, H. Winter, L. Petit, Phys. Stat. Solidi B 2001; **229** pp. 1459-1469.